

PATENT ABSTRACTS OF JAPAN

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(54) ROOM TEMPERATURE CURING COMPOSITION AND ITS PRODUCTION

(57)Abstract:

PROBLEM TO BE SOLVED: To produce a room temperature curing composition, comprising a specific polymer and a specified low-molecular polymer, having a sufficient low viscosity without deteriorating the flexibility of a cured product even when using an inorganic filler and useful as a sealing material, etc.

SOLUTION: This room temperature curing composition comprises (A) 100 pts.wt. polymer having 1-1.5 hydrolyzable silicon groups on the average in one molecule and 8000-50000 molecular weight and (B) 1-200 pts.wt. low-molecular polymer having 0.5-1.5 hydrolyzable silicon groups on the average in one molecule and 300-8000 molecular weight. Furthermore, both the main chains of the components (A) and (B) are essentially polyethers and the hydrolyzable silicon groups of the components (A) and (B) are represented by the formula $R_2-SiXaR_{13-a}$ [R1 is a 1-20C (substituted)monovalent organic group; R2 is a bivalent organic group; X is OH or a hydrolyzable group; (a) is 1-3]. The composition preferably contains further (C) a plasticizer, especially without containing a low-molecular one or preferably does not contain substantially the component (C).

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CLAIMS

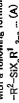
[Claim (s)]

[Claim 1] Aa opposed to polymer with an or more 8000 molecular weight [or less 50000] (I) and polymer (I) 100 weight section which averages in one molecule and has 1.5 or less one or more piece hydrolytic silicon groups. A room-temperature-curing nature constituent containing less than the with an or more 300 molecular weight [least than 8000] more than low molecular polymer (II) weight-section 200 weight section that averages in one molecule and has 1.5 or less 0.5 or more piece hydrolytic silicon groups.

[Claim 2] A room-temperature-curing nature constituent of Claim 1 whose both main chain of polymer (I) and chain of polymer (II) are polyether intrinsically.

[Claim 3] (I) 1 or 2 room-temperature-curing nature constituents by which both a hydrolytic

silicon group of polymer (I) and a hydrolytic silicon group of low molecular polymer (II) are expressed with a following formula (A).



R¹ is a univalent organic group substitution of the carbon numbers 1-20, or unsubstituted among a formula (A). R² is a divalent organic group. X is a hydroxyl group or a hydrolytic basis, and a is an integer of 1-3.

[Claim 4] Claim 1, a room-temperature-curing nature constituent of 2 or 3 in which a room-temperature-curing nature constituent does not contain a plasticizer substantially.

[Claim 5] Claim 1, a room-temperature-curing nature constituent of 2 or 3 which a room-temperature-curing nature constituent contains a plasticizer further, and do not contain a low molecule plasticizer as the plasticizer.

[Claim 6] Aa opposed to polymer (I) 100 with an or more 8000 molecular weight [or less 50000]

weight section which averages in one molecule and has 1.5 or less one or more piece hydrolytic silicon groups. A manufacturing method of a room-temperature-curing nature constituent making less than the with an or more 300 molecular weight [less than 8000] more than low molecular polymer (II) 1 weight-section 200 weight section that averages in one molecule and has 1.5 or less 0.5 or more piece hydrolytic silicon groups.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0061] [Field of the Invention] This invention relates to the room-temperature-curing nature constituent hardened under humectant-surface-moisture existence.

[0002] Description of the Prior Art The method of making harden various kinds of polymers which have an end hydrolytic silicon group, and using it for a sealing material, adhesives, etc., is known well, and is a useful method industrially.

[0003] The polymer especially whose main chain is polyether among such polymers is liquefied at a room temperature, and when a hardened material holds pliability also at low temperature comparatively end uses for a sealing material, adhesives, etc., it is provided with the desirable characteristic.

[0004]As a polymer of such hygroscopic-surface-moisture hardenability, the polymer of the hygroscopic-surface-moisture hardenability which has a hydrolytic silicon group is mentioned to and indicated to JP-3-759271, JP-3-478254, etc. In the polymer which has a hydrolytic basis at such end, although the pliability of a hardened material increases, the viscosity of resin becomes high and workability gets remarkably bad so that the molecular weight is generally large.

[0005] If the molecular weight of such a polymer is small, viscosity will become low, but a hardened material becomes a thing inferior to pliability. In order to make a polymer into hypoviscosity, maintaining the pliability of a hardened material until now, various kinds of plasticizers have been used.

[0066]As such a plasticizer, aromatic carboxylic acid ester, aliphatic-carboxylic-acid ester species, glycol ester, phosphoric ester, an epoxy plasticizer, a chlorinated paraffin, etc. are used. However, since these plasticizers are translatable, when it is used for a sealing material etc., there is a fault which has the surface contamination after contamination and paint of the ceiling part circumference and an adverse effect on an adhesive property.

[0007] The hardness constituent which adds the very low reactant plasticizer to the polymer of propyl 5-59261 A, without reducing the pliability of a hardened material to the polymer of the hygroscopic surface moisture hardenability which has a hydro-lytic silicon grain in order to cancel such a fault. However, in the use to a sealing material etc., pliability is higher, and when it paints on the surface in the good characteristic of elongation, the hardenability constituent in which surface stain resistance has been improved is called for. Although various kinds of elongating agents are used in combination with the hardness constituent, the plasticizing effect of the elongating agent is usually required for use of a building agent in order to harden the physical properties of a hardened material.

[0008] Problem(s) to be Solved by the Invention] Then, even if the viscosity of the hardenable composition could be reduced and it used the inorganic bulking agent, the hardened material with a flexibly good extension characteristic was given, and moreover, translatability was dramatically low, and as a result of examining the additive agent which does not pollute a surface coat, it resulted in this invention.

[Means for Solving the Problem] Namely, polymer with an or more 8000 molecular weight [or less 50000] (4) and polymer (1)100 weight section which averages this invention in one molecule and has

1.5 or less one or more place hydrolytic silicon groups is received. A room-temperature-curing reaction constituent containing less than the with an or more 300 molecular weight [less than 8000] more than low molecular polymer (I) weight-section 200 weight section that averages in one molecule, and has 1.5 or less 0.5 or more place hydrolytic silicon groups. And polymer (II) with an or more 8000 molecular weight [or less 50000] weight section which averages in one molecule and has 1.5 or less one or more place hydrolytic silicon groups is received, a manufacturing method of a room-temperature-curing reaction constituent mixing less than the with an or more 300 molecular weight [less than 8000] more than low molecular polymer (II) weight-section 200 weight section that averages in one molecule and has 1.5 or less 0.5 or more place hydrolytic silicon groups — it comes out.

[0101] [Embodiment of the Invention]As for both polymer (I)s and low molecule polymer (II)s that are used by this invention, consisting of polyether intrinsically is [the main chain of a molecule] preferred [0111]As for such a polymer, what is obtained by introducing a hydrolytic silicon group by the suitable method for a polymer containing hydroxyl group is preferred.

[0012] Such a polymer is proposed by JP 3-47825A, JP 3-72527A, JP 3-79627A, JP 46-30711B, JP 45-36319B, JP 46-17553B, etc. for example.

[013]A polyether containing hydroxyl group is obtained by polymerizing monooxide, such as bottom alkylene oxide of existence of an initiator and a catalyst.

[0014] The compound which has 1-10 active hydrogen as an initiator is preferred. As a compound which has 2-10 active hydrogen, a polyhydroxy compound is preferred, and the polyhydroxy compound has 2-4 hydroxy groups especially is preferred 2-6. Specifically Ethylene glycol, a diethylene glycol, propylene glycol, Dipropylene glycol, neopentyl glycol, 1,4-butanediol, There is polyol of low molecular weight from the object produced by making monomer react to 1,6-hexanediol, glycerin, trimethylolpropane, pentaerythritol, diglycerol, a shock sifoin, and these. One-third single use or two or more sorts of compound use may be sufficient as these.

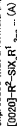
[0015] As a compound which has one active hydrogen, an unsaturation group content mono-hydroxy compound, for example like allyl alcohol is preferred. When manufacturing especially low molecular polymer (II), the aliphatic series of the carbon numbers 1-20, aliphatic fellows and an aromatic monosub, a thiol, secondary amine, carboxylic acid, etc. can be used.

[0016]As monooxide, there are propylene oxide, butylene oxide, ethylene oxide, allyl glycidyl ether, etc. Especially propylene oxide is preferred.

[0017]As a catalyst, catalyst, such as an alkaline metal catalyst, a composite metal cyanide complex catalyst, and metalloporphyrin, are mentioned.

[0018] Especially desirable polyethers containing hydroxyl group are polyoxypropylene diol, polyoxypropylene triol, polyoxypropylene tetraol, and polyoxypropylene hexaol. When using for following (1) or the method of (4), polyether of olefin ends, such as polyoxypropylene glycol monool, ether, can also be used.

[2019]The hydrolytic silicon group should just be a silicon group with which hydrolysis and crosslinking reaction occur with hygroscopic surface moisture. The silicon content group which has the hydrolytic basis coupled directly with the silicon atom can be used. For example, the basis expressed with a formula (A) is preferred.



[0021] R¹ is a divalent organic group the substitution of the carbon numbers 1-20, or unsubstituted among a formula (A). R² is a divalent organic group, X is a hydroxyl group or a hydrolytic basis, and a is an integer of 1-3.

[illegible]

ethoxy basis, a propoxy group, etc. can be illustrated, is an integer of 1-3 and 2 or 3 is preferred. [0024] Next, the manufacturing method of polymer (I) and (II) is explained. These polymers introduce a hydrolytic silicon group into the end of a polyether containing hydroxyl group by a method like following (1)-(4), and are manufactured.

(0025)(1) A method to which the silicon hydride compound expressed with what introduced the end group of hydroxyl group end polyether, and a formula (B) is made to react under existence of a catalyst. However B¹ in formula (B), X and a are the same also as a formula (A).

00267HSX R1 (R)

glass fiber, a glass filament, carbon fiber, the Kevlar textiles, and a polyethylene fiber.

[0052] As for especially the amount of the bulking agent used, 50 to 250 % of the weight is preferred ones to 1000% of the weight to the sum total of polymer (I) and low molecule polymer (II). These bulking agents may be used independently and may be used together two or more sorts.

[0053] A plasticizer may be used, although the room-temperature-curing nature constituent in this invention is fully immiscible in itself and it is preferred not to use a plasticizer substantially.

(2005) As a plasticizer, for example Diethyl phthalate, dibutyl phthalate, Phthalic acid alkyl ester, such as phthalic acid benzyl butyl ester; Diethyl adipate, Glucolol ester species, such as aliphatic-carboxylic acid benzyl butyl ester; pentaerythritol ester, such as succinic acid diisodecyl, dibutyl sebacate, and butyl oleate; Triethyl phosphate, Phosphoric ester, such as triethyl phosphate, epoxy plasticizer, chlorinated paraffin, such as epoxidized soybean oil and epoxy stearic acid benzyl, etc. can be independent or can use it with two or more sorts of mixtures.

[0055] However, as for a low molecular plasticizer has the problem which this invention of being easy to carry out after [room-temperature-curing nature constituent, hardening] bleed out, among such plasticizers, it is preferred to use it. That is, it is preferred for the room-temperature-curing nature constituent of this invention to contain a plasticizer further, and not to contain a low molecular plasticizer as the plasticizer. The compound itself is low molecular weight, and a low molecular plasticizer refers to the plasticizer which does not have a reactant group. For example, it is phthalic acid ethyl ester.

[0056] In the constituent of this invention, a hydrolytic silicon compound may be arbitrarily added in order to adjust physical properties and hardenability of a hardened material. As such a compound, specifically Tetramethyl silicate, vinyltrimethoxysilane, Although the compound etc, in which methyl trimethoxysilane, dimethylmethoxysilane, trimethylmethoxysilane, etc, these methoxy groups were replaced by the ethoxy groups is not illustrated, it is not limited to these.

[0057]As an additive agent, the photoresist compound aiming at adhesion grant agents, such as a thiocytroxy grant agent, phenol resin, an epoxy resin, etc. and various kinds of silane coupling agents, paints, various kinds of stabilizer, and surface treatment like oligoester acrylate etc. are mentioned. A solvent can also be used in order to prepare viscosity.

[0058] The room-temperature-curing nature constituent of this invention can be used as a sealing material especially an elastic sealing compound, and adhesives.

[0095] [Example] Although an example explains this invention below, this invention is not limited to these. Below, a part shows a weight section. As for the example of manufacture of low molecular polymer a-
d and Examples 5-8, working example of this invention and Examples 14-18 of the example of
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[0000]Example 1) Propylene oxide was made to react under existence of a zinc linox cycloalcanolate complex compound catalyst by having used 2-ethylhexanol as the inhibitor, and the polypropylene monomer was manufactured. Subsequently, after using 98% of terminal hydroxyl groups as an allyloxy group, methyldimethoxysilane of the equivalent was made to react 80% to the allyloxy group by having made chloroplatinic acid into the catalyst further, and the polymer of an molecular weight 5000 [about 1] which has a methyldimethoxy allyl propyl group was compounded. Viscosity was 1100cp at 25°C.

[0061] [Example 2] The bottom propylene oxide of existence of a zinc hexa cyanocobaltate complex compound catalyst was made to react by having used 2-ethylhexanol as the initiator, and polyoxypropylene monomer was manufactured. The methyl dimethoxy silyl propylsiloxanate of equimolar was made to react to this furthermore, and the polymer b of the molecular weight 4000

[0042] The compound was readily prepared by having used allyl alcohol as the initiator, and the polypropylene oxide of the molecular weight 2000 was manufactured. Then, it was used as the polyether chain group and the benzoyl chloride of oxanor under triethylamine existence. The reaction mixture was diluted with 5 times the amount, hexane, except for the triethylamine hydrochloride, hexane was distilled off and was rinsed, except the object of the benzoyloxy group. Next, it was made to react to methyl dimethoxysilane of the equivalent 80% to allyl group by having made chlorotriacetic acid into the catalyst, and the polymer of the molecular weight 2200 which has a methyl dimethoxy allyl propyl group was compounded.

Viscosity was 700cP at 25 °C.

[0063][Example 4] Propylene oxide was made to react by having used butanol as the initiator, and the polyoxypropylene monomer of the molecular weight 6000 was manufactured. After using 93% of terminal hydroxyl groups as an alkoxy group, the dimethylethoxy silane of the equivalent was made to react 95% to an allyl group, and the polymer d of the molecular weight 6000 [about 1 which has a dimethylethoxy siloxy group was compounded. Viscosity was 2500cP at 25 °C.

[0054] Example 5] Ethylene glycol was used as the initiator and the terminal hydroxyl groups of the polypropylene diol produced by making the bottom propylene oxide of a zinc hexa cyanocobaltate complex catalyst react was changed into the allyloxy group. Methyl dimethoxysilane was made to react by having made chloroplatinic acid into the catalyst furthermore, and the polymer A of the molecular weight 18000 [about] which has an average of 1.2 methyl dimethoxy alkyl groups per molecule at the end was compounded.

[0005]Example 6 Ethylene glycol was used as the initiator and the terminal hydroxyl groups of the polypropylene diol produced by making the bottom propylene oxide of existence of a zinc hexa cyanocobaltate complex compound catalyst react was changed into the allyloxy group. Methyl dimethoxysilane was made to react by having made chloroplatinic acid into the catalyst furthermore, and the polymer B of the molecular weight 18000 [about] which has an average of 1.7 methyl dimethoxy silyl methyl groups per molecule at the end was compounded.

[0066] Example 7) Glycerin was used as the initiator and the terminal hydroxyl groups of the polyoxypropylene triol produced by making the bottom propylene oxide of a zinc hexa cyanoosaltate complex catalyst react was changed into the allyloxy group. Methyl dimethoxysilane was made to react by having made chloroplatinic acid into the catalyst furthermore, and the polymer C of the molecular weight 19000 [about 1] which has an average of 1.8 methyl dimethoxy allyl group per molecule at the end was compounded.

[0077] Example 8] Glycerin was used as the initiator and the terminal hydroxyl groups of the polyoxypropylene triol produced by making the bottom propylene oxide of existence of a zinc hexa cyanocobaltate complex catalyst react was changed into the allyloxy group. Methyl dimethoxysilane was made to react by having made chloroplatinic acid into the catalyst furthermore, and the polymer D of the molecular weight 19000 [about] which has an average of 2.4 methyl dimethoxy allyl propyl groups per molecule at the end was compounded.

[0088][E-sample 9] Glyocerin was used as the initiator and the terminal hydroxyl groups of the polyoxypolyene triol produced by making the bottom propylene oxide of existence of a zinc hexa cyanoaluminate complex catalyst react was changed into the allyloxy group. Methyl dimethoxysilane was made to react by having made chloroplatinic acid into the catalyst furthermore, and the polymer E of the molecular weight 30000 [about.] which has an average of 2.4 methyl dimethoxy allyl propyl groups per molecule at the end was compounded.

[0059] Examples 10–18: Polymer A-E and low molecule polymer a-d (or dioctyl phthalate: DOP) were mixed at a rate of the description to Table 1, mixed liquor was obtained, and the viscosity (a unit is cP) at 25 °C was measured. P-Si shows the number of the hydrolytic silicon groups per molecule of a polymer among front.

[0070] As opposed to these 160 copies of mixed resin — calcium carbonate (Shiroishi calcium company make), 75 copies of Hakuren CO., 75 copies of calcium carbonate (Shiroishi calcium company make), HOWATON SEI, 30 copies of titanium dioxides, and stabilizer (the mixture of an antioxidant, an ultraviolet absorber, and light stabilizer) the Chiba-Gunji make, about B192 copy and a phobate-styrene resin (the registered chemical industry Co., Ltd. make). It treated the compound and dried it at 80°C for 2 h.

[0071] The mixed resin was composed of two copolymers of styrene and ethyl acrylate (St-EA-Copoly Co., Ltd. make #KMS300), one copy of hydrogenation catalyst oil, and two copies of dibutyl tin oxide (DIBUTYL TIN OXIDE, Nippon Kagaku Sangyo Co., Ltd. make, NASENUSUZU), and moisture does not mix, and was considered as the uniform mixture.

[0072] The mixed resin was pierced with the JIS No. 3 dumbbell after creating the sheet about 2 mm thick and curing out cure for seven days at 20 ± 5 °C subsequently for seven days at 20 ± 5 °C modulus

(M_{50} , units/kg/cm²) and breaking strength (unit: kg/cm²) — it was extended and (%) was measured [0072]. After having applied the solvent system alkyl paint (the Rock Paint Co., Ltd. make, house paint) after creasing and carrying out cure of the sheet about 1 cm thick, and heating for one week at 70 °C, it was exposed to the outdoors and the diff. situation of the paint surface was observed one

month afterward, evaluation → O: --- it was assumed that adhesion of a beautiful thing, dust, etc., is remarkable and dry although dirt has adhered a little (stain resistance of a paint surface).

[0073]x which has pliability suitable as O: **** modulus sealing material for the pliability of a hardened material in which carried out cure of this mixture and it was obtained. It presupposed that it is too hard as a 1 **** modulus sealing material, and evaluated. These results are also collectively shown in Table 1.

[0074]

[Table 1]

例	10	11	12	13	14	15	16	17	18
A	70	70	70	70	70	70	70	70	70
B	30	30	30	30	30	30	30	30	30
C	30	30	30	30	30	30	30	30	30
D	30	30	30	30	30	30	30	30	30
E	30	30	30	30	30	30	30	30	30
F-31	1.38	1.38	1.38	1.38	1.38	1.38	1.38	1.38	1.38
配合体	60	60	60	60	60	60	60	60	60
a	60	60	60	60	60	60	60	60	60
b	60	60	60	60	60	60	60	60	60
c	60	60	60	60	60	60	60	60	60
d	60	60	60	60	60	60	60	60	60
DOP									
粘度	9700	9600	9500	10000	9600	15000	7000	7000	29200
Mn	1.0	1.1	1.3	0.9	1.9	2.5	0.8	1.7	2.0
溶解度	5.8	6.0	6.5	5.6	8.3	9.5	5.5	7.9	8.5
伸 び	830	810	790	850	750	650	820	770	750
機械強度	○	○	○	○	○	○	×	×	○
の耐熱性	○	○	○	○	×	×	×	×	×
劣化性	○	○	○	○	×	×	×	×	×

[0075]

[Effect of the Invention]Even if the room-temperature-curing nature constituent of this invention has low viscosity enough and it uses an inorganic bulking agent, the pliability of a hardened material is not reduced. And since the low molecule polymer used by this invention has very low translatability, when the constituent of this invention is used for a sealing material etc., it does not have contamination or the adverse effect to an adhesive property of the ceiling part circumference or a paint surface.

[Translation done.]

weight section which averages in one molecule and has 1.5 or less one or more piece hydrolytic silicon groups. A manufacturing method of a room-temperature-curing nature constituent polymer (II) than the with an or more 300 molecular weight [less than 8000] with more low molecule polymer (II) 1 weight-section 200 weight section that averages in one molecule and has 1.5 or less 0.5 or more piece hydrolytic silicon groups.

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CORRECTION OR AMENDMENT

CORRECTION OR AMENDMENT

[Section Type] The 3rd Type of the part III gate

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[Data of Publication] Heisei 9(1997) April 8 (1997.4.8)

[Application number] Japanese Patent Application No. 7-254030

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conv. = free vol.

23

may 5/54 you

PH [stop pulling]

Amendment 1

[Method of Amendment] Change

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[C:\aim(c)]
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[Claim 1]As opposed to polymer with an or more 8000 molecular weight [or less 50000] (I) and polymer (II)one weight section that averages in one molecule and has 1.5 or less one or more piece hydrolytic silicon groups. A room-temperature-curing nature constituent containing less than the hydrolytic silicon weight [less than 8000] more than low molecular polymer (III) weight- with an or more 300 molecular weight [less than 8000] more than low molecular polymer (III) weight- section 200 weight section that averages in one molecule and has 1.5 or less 0.5 or more piece hydrolytic silicon groups.

[Claim 2] The room-temperature-curing nature constituent according to claim 1 whose both main chain of polymer (I) and main chain of low molecule polymer (II) are polyether intrinsically,

[Claim 3] The room-temperature-curing nature constituent according to claim 1 or 2 in which a room-temperature-curing nature constituent does not contain a plasticizer substantially.

[Claim 4] The room-temperature-curing nature constituent according to claim 1 or 2, which a room-temperature-curing nature constituent does not contain a photo-curing nature constituent.

temperature-curing nature constituent contains a plasticizer further, and does not contain a low molecule plasticizer as the plasticizer.

[Claim 5]As opposed to polymer (I)100 with an or more about molecular weight 1 or less about 1

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http://www4.ipdl.inp.it/go.jp/cgi-bin/tran_web.cgi/eije?stw_u=http%3A%2F%2Fwww4.ipdl.i... 2010/08/05

compounded. Viscosity was 700cP at 25 °C.

[Translation done.]